

AFML-TR-64-417

PART II

ADDO 51752

OFFICIAL FILE COPY

**NITROGEN-PHOSPHORUS POLYMERS***MARGOT BECKE-GOEHRING**UNIVERSITY OF HEIDELBERG*

TECHNICAL REPORT AFML-TR-64-417, PART II

NOVEMBER 1966

Distribution of this document is unlimited

OFFICIAL FILE COPY

AIR FORCE MATERIALS LABORATORY  
RESEARCH AND TECHNOLOGY DIVISION  
AIR FORCE SYSTEMS COMMAND  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

20040219335

Best Available Copy

## NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Copies of this report should not be returned to the Research and Technology Division unless return is required by security considerations, contractual obligations, or notice on a specific document.

AFML-TR-64-417  
PART II

## **NITROGEN-PHOSPHORUS POLYMERS**

*MARGOT BECKE-GOEHRING*  
*UNIVERSITY OF HEIDELBERG*

**Distribution of this document is unlimited**

## FOREWORD

This report was prepared by the Anorganisch-Chemisches Institut, University of Heidelberg, Heidelberg, Germany under Contract AF 61(052)-682. The contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena", Task No. 734201, "Basic Factors on the Synthesis of Macromolecular Material". The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, Dr. W. L. Lehn, Project Engineer.

This report covers work conducted from 1 October 1964 through 30 June 1966. The manuscript was released by the author in June 1966 for publication as a technical report.

This technical report has been reviewed and is approved.



WILLIAM E. GIBBS  
Chief, Polymer Branch  
Nonmetallic Materials Division  
Air Force Materials Laboratory

ABSTRACT

A variety of chemical systems containing phosphorus nitrogen bands have been investigated as potential intermediates for the synthesis of polymeric materials having extreme thermal and chemical stability. These investigations include the preparation and reactions of a variety of compounds with four-membered ring systems containing alternate P and N atoms, compounds with four-membered ring systems containing P, N and C atoms, and compounds containing P-N-P chains; and the preparation of phosphonitrilic chlorides and their derivatives.

## TABLE OF CONTENTS

SECTION	PAGE
I INTRODUCTION	1
II COMPOUNDS WITH FOUR-MEMBERED RING SYSTEMS CONTAINING P AND N	2
A. 2, 2, 2, 4, 4, 4-Hexachloro-1, 3-Dimethylcyclodiphosphazane (V)	14
B. 2, 4-Dioxo-2, 4-Dichloro-1, 3-Dimethylcyclodiphosphazane (VII)	14
C. 2, 4-Dithio-2, 4-Dichloro-1, 3-Dimethylcyclodiphosphazane (VIII)	15
D. 2, 4-Dithio-2, 4-Dianilino-1, 3-Dimethylcyclodiphosphazane (IX)	15
E. 2, 4-Dithio-2, 4-Bis-Diethylamino-1, 3-Dimethylcyclodiphosphazane (X)	16
F. N-Methylimidodithiophosphoric Tetra-N-Methylamide (XI)	16
G. 2, 4-Dithio-2, 4-Bis-N-Methylamino-1, 3-Dimethylcyclodiphosphazane (XII)	16
H. $P_4(NCH_3)_6Cl_8$ (XXII)	16
I. $P_4(NCH_3)_6O_2Cl_4$ (XXIV)	17
J. $P_4(NCH_3)_6S_2Cl_4$ (XXIII)	17
III COMPOUNDS WITH FOUR-MEMBERED RING SYSTEMS CONTAINING P, N AND C	19
A. Preparation of Compound XXV	20
IV COMPOUNDS WITH P-N-P CHAINS	21
A. $[(C_6H_5)_2P(Cl)-NH_2]Cl$ (LX)	29
B. Preparation of $[(C_6H_5)_2P(Cl)=N-PCl_3]PCl_6$ (XXXII)	29
C. Preparation of $[(C_6H_5)_2P(Cl)=N-PCl_3]Cl$ (XXXIII)	29
D. Preparation of $(C_6H_5)_2P(Cl)=N-P(O)Cl_2$ (XLIII)	30
E. Preparation of $(C_6H_5)_2P(O)-NH-P(O)(OH)_2$	30
F. $[(C_6H_5)_2PN]_3$ (LXI) and $[(C_6H_5)_2PN]_4$ (LXII)	30
G. Infrared Spectra	31
V PHOSPHONITRILIC CHLORIDES $(NPCl_2)_n$ AND DERIVATIVES	32

## SECTION I

### INTRODUCTION

The purpose of the work covered by this report was the preparation of phosphorus nitride derivatives. The work was divided into four sections.

Section II Compounds with 4-Membered Ring Systems Containing P and N

Section III Compounds with 4-Membered Ring Systems Containing P, N and C

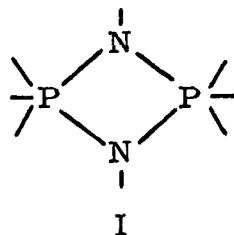
Section IV Compounds with P-N-P Chains

Section V Phosphonitrilic Chlorides  $(\text{NPCl}_2)_n$  and Derivatives

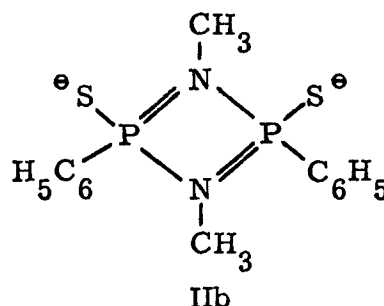
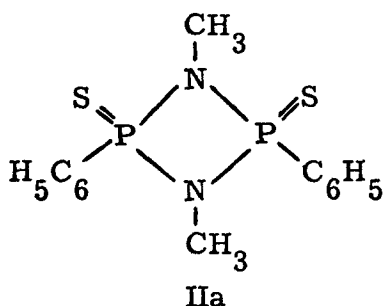
## SECTION II

### COMPOUNDS WITH FOUR-MEMBERED RING SYSTEMS CONTAINING P AND N

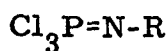
First, we studied phosphorus-nitrogen compounds containing ring systems. Various phosphorus-nitrogen compounds are known (Reference 1) which comprise a four-membered ring system of the type indicated by formula I.



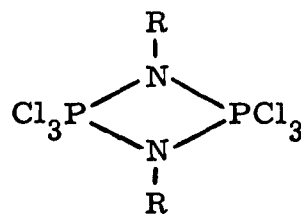
A series of such compounds has been prepared by Michaelis (Reference 2). It was found, for example, that the compound  $[C_6H_5NP(O)C_6H_5]$  is dimeric and this fact would suggest that a tetracyclic system corresponding to formula I might apply for this substance. This formulation was justified by Trippett (Reference 3) for the compound  $[CH_3NP(S)C_6H_5]_2$  on the basis of nuclear magnetic proton-resonance spectra. Accordingly, formula II can be ascribed to this compound. From the infrared spectrum, Trippett assumed that resonance exists between the forms IIa and IIb.



Substances with the basic structure I are also obtained in the reaction of phosphorus pentachloride with primary amines (Reference 1), whereby compounds of type III or IV can be prepared. Products of type IV are preferred when strongly basic amines (amines in which the basic constant of the aqueous solution lies between  $10^{-4}$  and  $10^{-9}$ ) are employed (Reference 4) and the hydrochloride of such an amine is treated with  $PCl_5$  in an inert solvent.



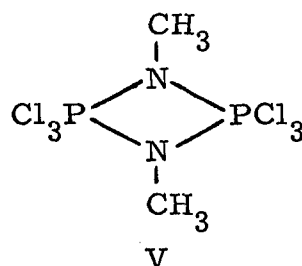
III



IV

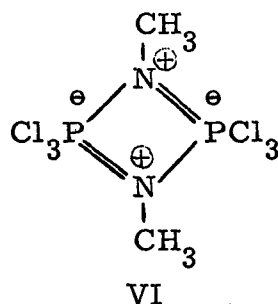
One of the most thoroughly investigated substances of type IV is compound V, which was first prepared by Chapman, Holmes, Paddock, and Searle (Reference 5).





All the phosphorus atoms in this compound are chemically equivalent, since the  $P^{31}$  NMR spectrum of a solution of the substance in  $CHBr_3$  reveals only one signal (Reference 6) with a chemical shift 78.2 ppm (referred to 85% phosphoric acid as standard). The strongly positive chemical shift shows that 5-coordinate phosphorus is contained in this compound. This is further supported by a comparison with  $PCl_5$ , whose solution in carbon disulfide gives rise to a peak at +80 ppm. Moreover, the proton-resonance spectrum found by Trippett (Reference 3) is in agreement with formula V.

The P-N bond strengths in V have been estimated by Fowell and Mortimer (Reference 7); these authors found the value 74.3 kcal/mole for these linkages. The P-N bond in the tetracyclic system V would thus appear to be stronger than in the case of the normal P-N single bond, for which 66.8 kcal/mole was determined from studies of  $P[N(C_2H_5)_2]_3$ . It is very probable that these differences do not arise from a difference in hybridization of the phosphorus atoms, and it would seem reasonable to assume that in 2, 2, 2, 4, 4, 4-hexachloro-1, 3, -dimethylcyclophosphazane further stabilization by means of  $d_{\pi}p_{\pi}$  bonds occurs in the manner indicated by formula VI.



The structure of this compound was elucidated by Hess and Forst (Reference 8). Figure 1 shows the result of this investigation.

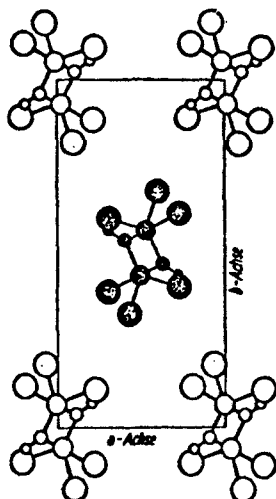


Figure 1. Crystal Structure of VI, Projection on  $[001]$

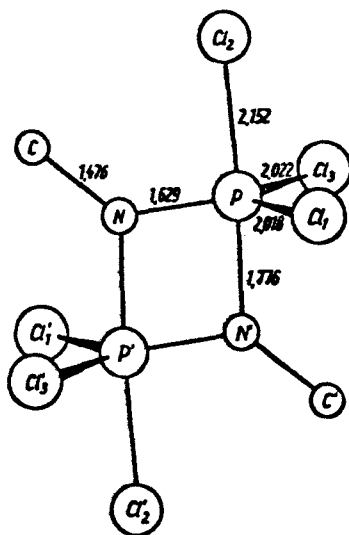


Figure 2. Compound VI,  
Atom Distances Å

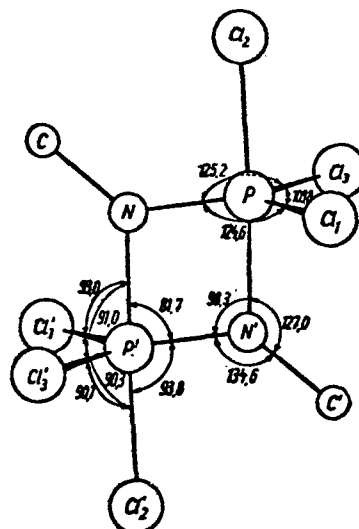
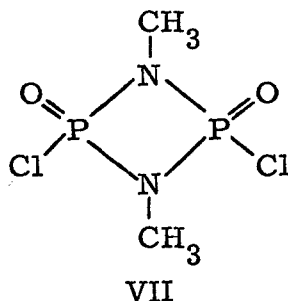
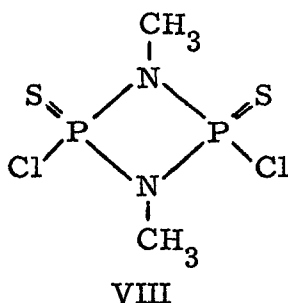


Figure 3. Compound VI,  
Bond Angles

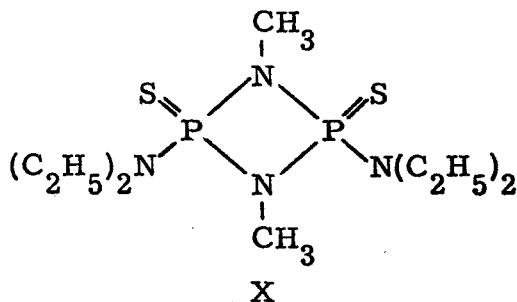
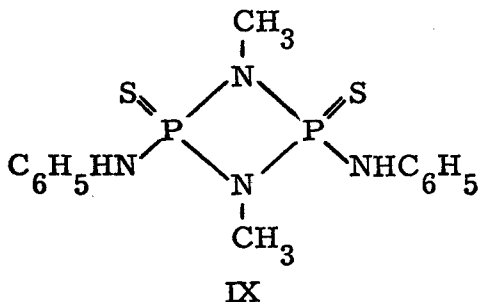
It appeared likely that compounds V and VI would provide a basis for the conversion of 5-coordinate phosphorus into the 4-coordinate state. Toward this end, we treated the substance with sulfur dioxide and were able to obtain compound VII in excellent yield. VII is colorless and crystalline; it is extremely sensitive to moisture and hydrolyzes rapidly. The compound dissolves readily in benzene, and the  $P^{31}$  NMR spectrum of the solution reveals a single peak at +5.3 ppm. This result shows that in this case also, all the phosphorus atoms in the molecule are chemically equivalent. Comparison with other phosphorus compounds (Reference 6) indicates clearly that the phosphorus atoms in VII are 4-coordinate.



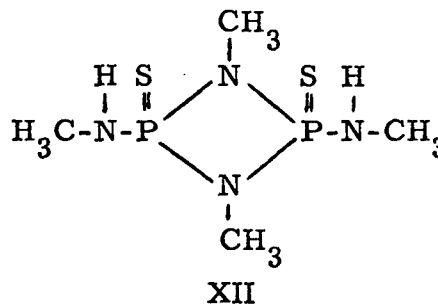
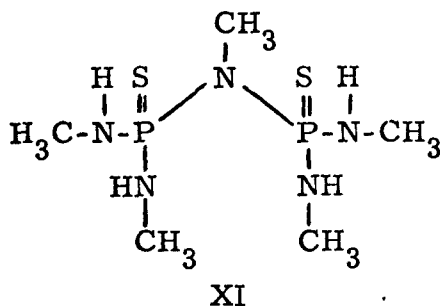
We then attempted to prepare the sulfur compound analogous to VII by reacting 2, 2, 2, 4, 4, 4-hexachloro-1, 3-dimethylcyclophosphazane (V) with  $\text{H}_2\text{S}$  at room temperature. When dry pyridine was added to the reaction mixture, 2, 4-dithio-2, 4-dichloro-1, 3-dimethylcyclophosphazane (VIII) was formed in excellent yield together with pyridinium chloride; VIII also proved to be crystalline and sensitive to hydrolysis. Its  $\text{P}^{31}$  NMR spectrum in benzene showed one resonance signal at  $-51.5$  ppm. These observations are in accord with the structural formula VIII. It has been generally observed that 4-coordinate phosphorus which bears a sulfur atom as one of its ligands gives rise to an NMR signal in this range, indicating that the phosphorus atoms in such compounds are only weakly shielded (Reference 9).



It was found that VIII reacted smoothly with amines. Compound IX was obtained by the action of a solution of aniline in benzene at room temperature. The corresponding diethylamine compound X was prepared in a similar way.



On the other hand, the reaction with excess monomethylamine in the absence of a solvent at  $-50^\circ\text{C}$  resulted in cleavage of the four-membered ring and formation of N-methylimidodithiophosphoric tetra-N-methylamide (XI). When heated in vacuum (15 mm Hg) at  $180^\circ$  to  $200^\circ\text{C}$ , this product split off methylamine to regenerate the tetracyclic compound XII.



In all of these sulfur-containing compounds the phosphorus nuclei are only weakly shielded. This is clearly shown by the  $P^{31}$  NMR spectra; for example, IX (in dichloroethane) has a chemical shift of -54 ppm, XII (in benzene) indicates -60 ppm, and X (in methylene chloride) -63 ppm. These data would suggest that it is not strictly correct to incorporate a P=S double bond in the formulation of these compounds; rather, the bond would appear to be strongly polar and can be better represented by the form  $P^{\delta+}-S^{\delta-}$ .

The structure of compound VIII was elucidated by X-ray investigation. Figure 4 shows the result.

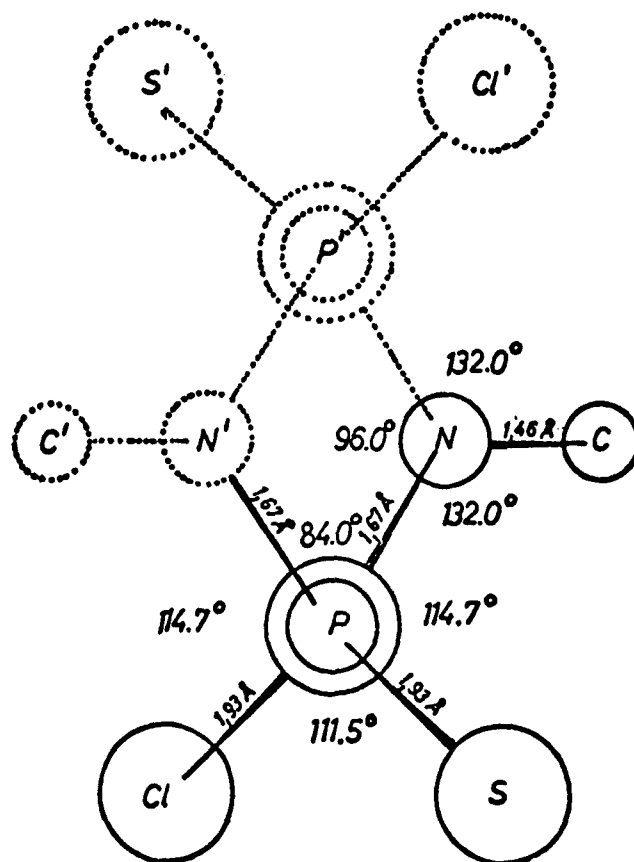
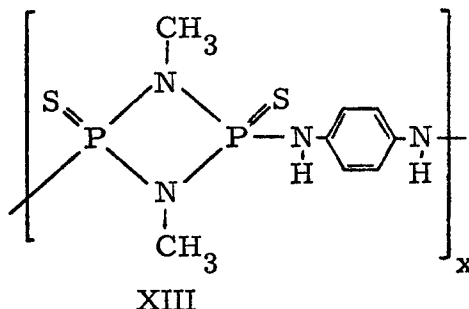


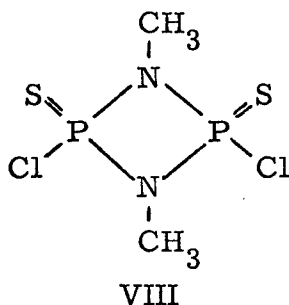
Figure 4. Structure of Compound VIII With Bond Angles and Bond Length (The ring is planar.)

## Part II

Following the successful preparation of compound IX, it appeared expedient to react VIII with diamines under the same conditions which led to substitution in the case of the conversion of VIII into IX. Accordingly, a reaction with paraphenylene diamine was carried out, which furnished XIII, a nonhygroscopic solid.



Accordingly, some time was devoted to the preparation of polymers utilizing compound VIII and diamines as the starting materials.



These reactions were carried out with hexamethylene diamine, ethylene diamine, hydroquinone, p-phenylene diamine, and silver cyanamide.

Ethylene chloride was employed as solvent for the reaction of VIII with hexamethylene diamine. The reaction was exothermic and led to the product  $[P_2N_4S_2C_8H_{20}]_x$ . This polymer was found to be insoluble in most solvents (including water) but it dissolved slightly in warm dimethylsulfoxide. The substance became thermoplastic and malleable at 180°, but at 220° it began to decompose.

By treating VIII with ethylene diamine in a solution of carbon tetrachloride, we were able to obtain the compound  $[P_2N_4S_2C_4H_{12}]_x$  in good yield. This material was stable up to 260° but the malleable state was not attained before decomposition set in. As in the previous instance, the substance proved to be insoluble in water, methanol, acetone, and other common solvents, indicating slight solubility only in dimethylsulfoxide.

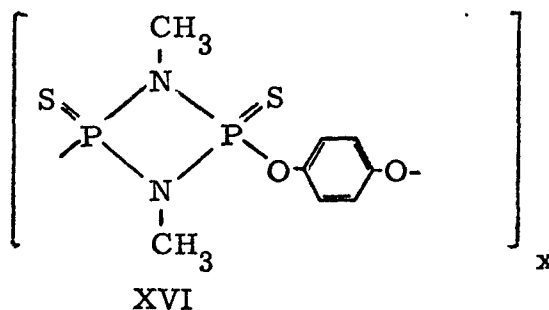
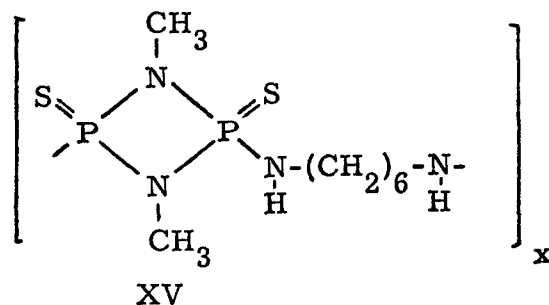
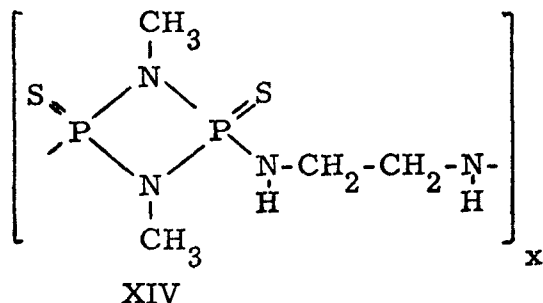
Reaction of VIII with hydroquinone in a mole ratio of 1:1 furnished  $[P_2N_2S_2O_2C_8H_{10}]_x$ . In this case, the reactants were mixed directly and heated to 190° in the absence of a solvent. The mixture fused and the melt evolved HCl, whereupon it rapidly became viscous. The material finally solidified to a yellowish-white substance, from which unreacted hydroquinone was subsequently removed by washing with ether. The polymer was stable up to 330° and did not exhibit thermoplastic properties at any temperature. This substance did not dissolve in water, methanol, acetone or other solvents excepting dimethylsulfoxide and dioxane, in which it was slightly soluble.

When VIII was reacted with hydroquinone in a mole ratio of 1:2, a frothy solid mass was produced which revealed a somewhat higher degree of thermal stability than that of the product obtained in the case of the reaction in a 1:1 mole ratio. Further studies with the "frothy" material are in progress.

The reaction of VIII with p-phenylene diamine in ethylene chloride was exothermic and led to a white solid product having the composition  $[P_2N_4S_2C_8H_{12}]_x$ . However, this substance was not obtained pure, and could not be freed from accompanying p-phenylene diamine hydrochloride.

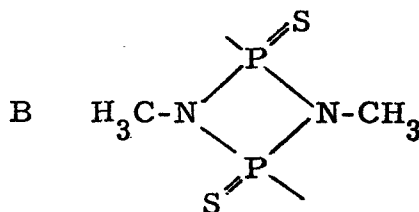
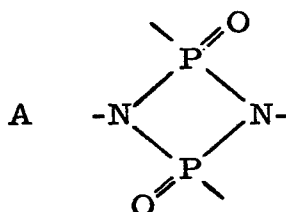
$Ag_2NCN$  did not react with compound VIII in the presence of a solvent; however, reaction occurred when the components were mixed directly and fused. Solid polymeric products were formed which are presently being investigated.

The infrared spectra of all these products indicate that the ring system present in VIII is retained in all instances; the absorption bands which are characteristic for the four-membered ring system were observed in the spectrum of each of the polymers. It was also evident that the diamines reacted in the expected manner, that is, one molecule of diamine per molecule of the cyclic compound VIII. Apparently, polymer chains containing the four-membered ring are produced which are then linked via amino groups XIV, XV. The establishment of an  $-O-C_6H_4-O-$  bridge between two four-membered ring systems as in XV, is also possible.

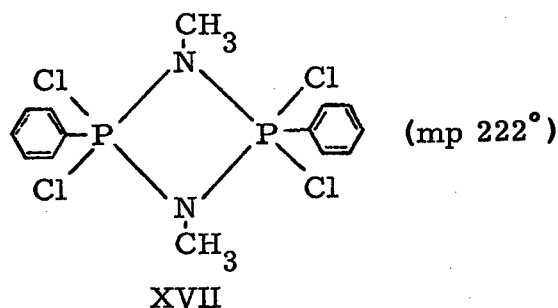


## Part II

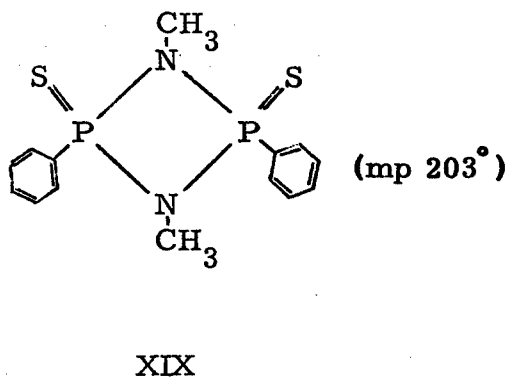
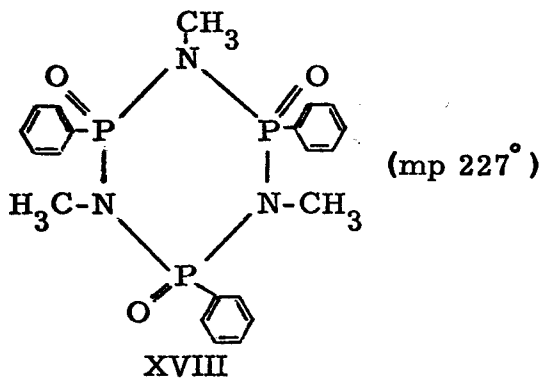
All these compounds with the units B may be compared with the DAPO-derivatives with the unit A which were prepared by Parts, Nielsen and Miller (Reference 10).



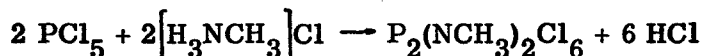
Another type of derivatives of the ring system I was obtained when  $\text{C}_6\text{H}_5\text{PCl}_4$  was used instead of  $\text{PCl}_5$  as reactant. When  $\text{C}_6\text{H}_5\text{-PCl}_4$  and  $[\text{CH}_3\text{NH}_2]\text{Cl}$  were reacted, substance XVII was formed.



We have studied the reaction of XVII with  $\text{SO}_2$ . A compound  $\text{C}_6\text{H}_5\text{P(O)NCH}_3$  was formed which is trimeric in the cold XVIII. With  $\text{H}_2\text{S}$ , however, compound XIX was obtained.



Many of these phosphorus-nitrogen compounds incorporating a four-membered ring system according to I were obtained starting with the reaction of  $\text{PCl}_5$  with primary amine. Closer study of this reaction system revealed that V is the main product although a further crystalline substance can be isolated from the mother liquors. Thus the principal reaction, leading to the tetracyclic compound V, can be expressed by the equation



whereby the following reaction can also participate:

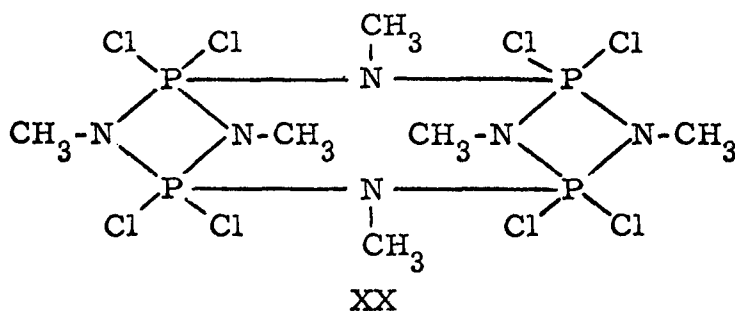


The new compound is produced from  $\text{PCl}_5$  and methylammonium chloride in a yield of 2 to 4 percent based on  $\text{PCl}_5$ ; it can be recrystallized from larger amounts of benzene and melts with decomposition at  $395^\circ$  in a sealed tube.

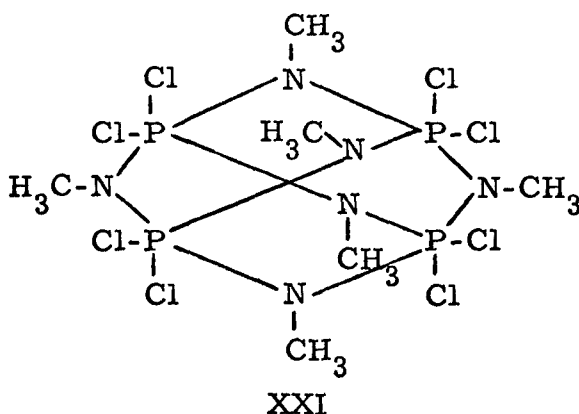
Ebullioscopic molecular weight determinations in benzene and indichloroethane were carried out in an attempt to elucidate the structure of this substance. The value found was 584, which would indicate that the formula employed in the above equation is correct.

The  $\text{P}^{31}$  NMR spectra of solutions of the compound in benzene and in pyridine revealed only one resonance signal at +74.5 ppm. It can be inferred from this result that 5-coordinate phosphorus is present in the compound and that the phosphorus atoms are either chemically equivalent or that they are at least situated in chemically similar environments.

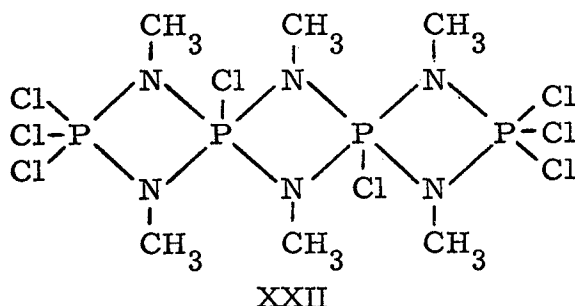
Accordingly, formulae XX, XXI or XXII may be considered for  $\text{P}_4(\text{NCH}_3)_6\text{Cl}_8$



The NMR spectrum and the high melting point appeared to support formula XXI (Reference 11), although the infrared spectra were more in accord with XX and XXII. By comparison, Chapman et al., found the following infrared bands for V: 434m, 575s, 658s, 700m, 747vw, 847vs, 1162s, 1184s, 1210s, 1439m, 1461m, 2812w, 2941m, 2996m ( $\text{cm}^{-1}$ ).



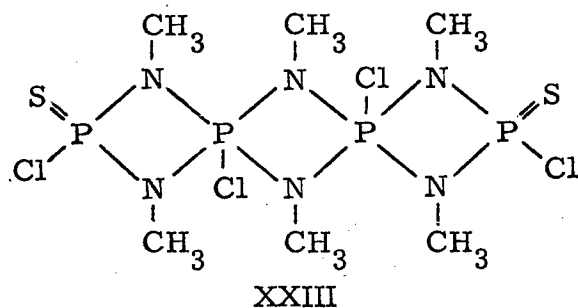




In addition to these bands, we observed absorption at  $920\text{ cm}^{-1}$  (m) and at  $1290\text{ cm}^{-1}$  (m). In contrast to Chapman et al., we employed KBr for the sample pellet.

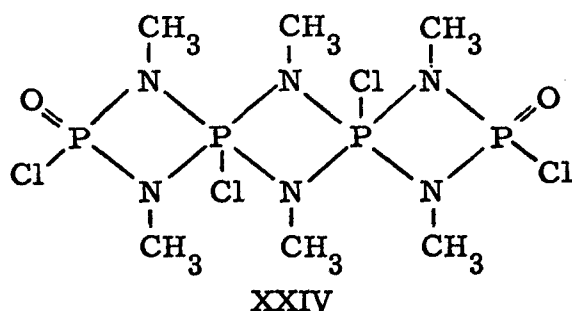
Corresponding infrared studies of  $\text{P}_4(\text{NCH}_3)_6\text{Cl}_8$  revealed bands at  $2960$  and  $2820\text{ cm}^{-1}$ , which can be ascribed to C-H and N-CH vibrations, respectively. We also found further bands at  $1460\text{m}$ ,  $1425\text{m}$ ,  $1235\text{s}$ ,  $1215\text{vs}$ ,  $1187\text{vs}$ ,  $1170\text{vs}$ ,  $877\text{s}$ ,  $843\text{s}$ ,  $715\text{s}$ , and  $654\text{s}$  ( $\text{cm}^{-1}$ ). The spectra of V and  $\text{P}_4(\text{NCH}_3)_6\text{Cl}_8$  display a number of similar features, particularly with respect to a common, very strong absorption at  $850\text{ cm}^{-1}$  which can be ascribed to the P-N vibration and which is attributed by Trippett to the tetracyclic phosphorus-nitrogen system. It therefore seemed feasible that the new compound might also consist of a phosphorus-nitrogen four-membered ring system, suggesting formulae XVI and XVIII.

Additional structural studies were carried out with the help of chemical reactions. First, the interaction of  $\text{P}_4(\text{NCH}_3)_6\text{Cl}_8$  and  $\text{H}_2\text{S}$  in pyridine was investigated. The product was a pale yellow, crystalline solid with the composition  $\text{P}_4(\text{NCH}_3)_6\text{S}_2\text{Cl}_4$ . The  $\text{P}^{31}$  NMR spectrum of a solution of this substance in dichloroethane was characterized by one resonance maximum at  $-55.3\text{ ppm}$  and another of equal intensity at  $+68\text{ ppm}$ . This result shows that the compound contains two types of phosphorus atoms which are chemically nonequivalent. Half of the P atoms are linked to sulfur and are 4-coordinate (corresponding to the signal at  $-55.3\text{ ppm}$ ); the remaining P atoms are 5-coordinate, giving rise to the resonance peak at  $+68\text{ ppm}$ . On this basis, formula XXIII was ascribed to the compound.



The fact that  $\text{P}_4(\text{NCH}_3)_6\text{Cl}_8$  could not be made to react with more than two moles of  $\text{H}_2\text{S}$  provided strong support for formula XXII as a correct representation of  $\text{P}_4(\text{NCH}_3)_6\text{Cl}_8$ . Treatment of  $\text{P}_4(\text{NCH}_3)_6\text{Cl}_8$  with  $\text{SO}_2$  led to the crystalline substance  $\text{P}_4(\text{NCH}_3)_6\text{O}_2\text{Cl}_4$  in high

yield. The  $P^{31}$  NMR spectrum of a solution of this product in pyridine contained peaks of equal intensity with the chemical shifts +73 ppm and -4 ppm. This result speaks unequivocally for formula XXIV.



These results could be proved by X-ray analysis. These results, obtained with compound XXII are shown in Figures 5 and 6. In Figure 7 the environment of phosphorus  $P_2$  is shown in detail. Figure 8 allows a comparison with the phosphorus atom in  $PCl_5$ .

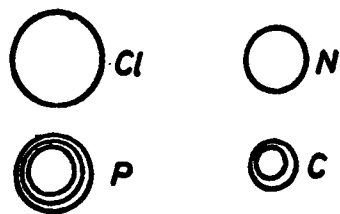
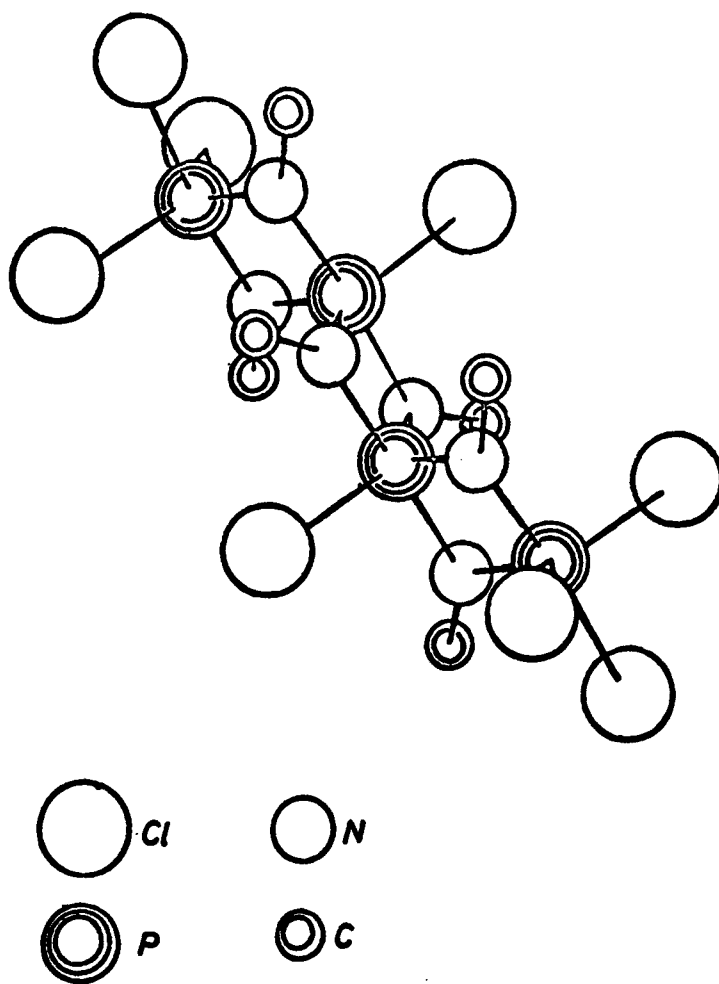


Figure 5. Structure of Compound XXII

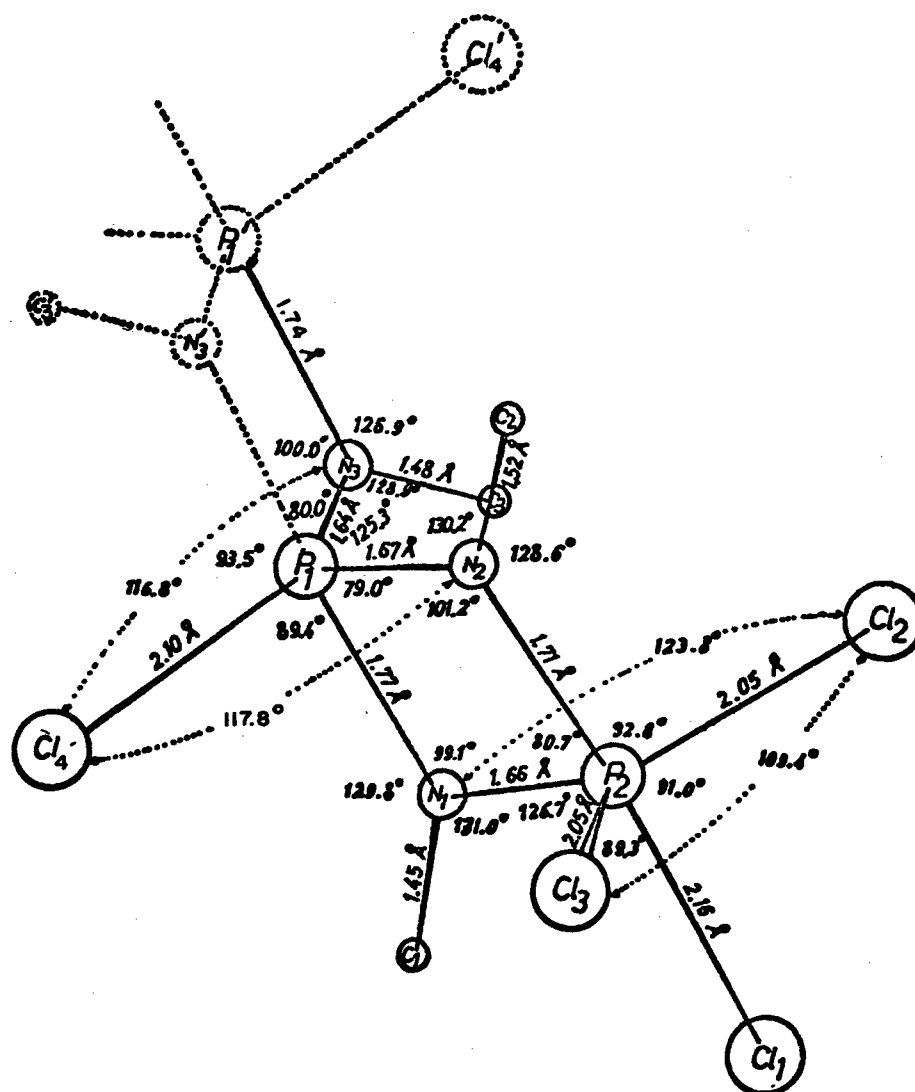


Figure 6. Part of the Molecule of XXII With Bond Lengths and Bond Angles

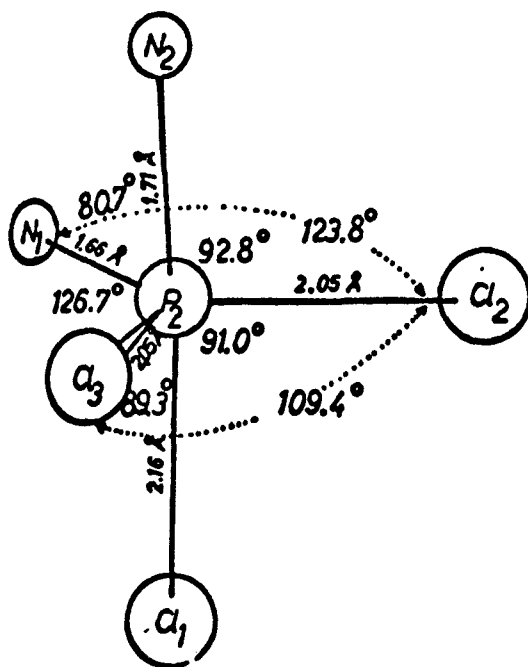
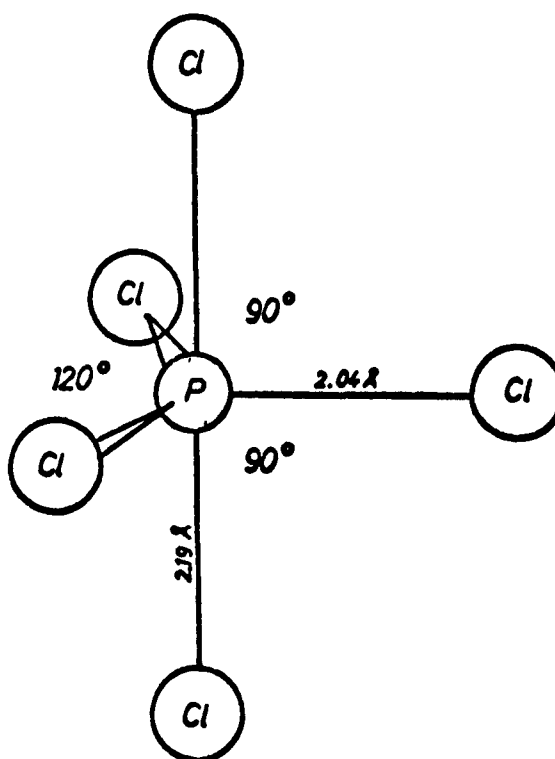


Figure 7. Part of the Molecule of XXII

Figure 8.  $\text{PCl}_5$ 

## A. 2, 2, 2, 4, 4, 4-HEXACHLORO-1, 3-DIMETHYLCYCLODIPHOSPHAZANE (V)

A mixture of 74.3 g of methylammonium chloride (1.1 mole) and 208.5 g of  $\text{PCl}_5$  (1 mole) was placed in 750 ml of dry tetrachloroethane and heated to boiling. Evolution of  $\text{HCl}$  set in at  $60^\circ$  and continued for about 6 hours. After this time the solution was allowed to cool to about  $40^\circ$  and then concentrated in a thin-layer evaporator under partial pressure (20 mm Hg) until crystals appeared. The mixture was then cooled to  $0^\circ$  and the crystals filtered off. The yield of V is about 150 g, corresponding to 90 percent of theory. The product can be recrystallized from benzene,  $\text{CCl}_4$ , di- and tetrachloroethane, and acetonitrile. With the latter solvent and repeated recrystallization, it is possible to obtain a sample which melts at  $178^\circ$  (uncorr) as opposed to the melting point of  $160^\circ$  reported by Chapman et al. (Reference 5). It is essential that the melting point determination be carried out in a sealed tube. In all other aspects, this substance is identical with that obtained by the authors mentioned above (Reference 5).

## B. 2, 4-DIOXO-2, 4-DICHLORO-1, 3-DIMETHYLCYCLODIPHOSPHAZANE (VII)

A total of 100 g of  $\text{P}_2(\text{NCH}_3)_2\text{Cl}_6$  (V) was dissolved in 500 ml of dry methylene chloride; dry  $\text{SO}_2$  was then passed into the cooled solution (ice bath) with stirring. At first, a portion of the starting material remained undissolved, but this was consumed in the course of the reaction.  $\text{SO}_2$  is sparged into the clear, colorless solution until approximately twice the theoretical amount has been absorbed. The reaction mixture is then allowed to stand at  $0^\circ$

## Part II

overnight, after which the solvent is removed in a thin-layer evaporator under aspirator vacuum. The residue consists of a pale yellow oil which soon crystallizes; this product can be recrystallized from cyclohexane or, preferably, sublimed at  $60^{\circ}/0.01$  mm Hg. The melting point is unsharp ( $101^{\circ}$ - $103^{\circ}$ ). Yield: 92.5 percent, based on  $P_2(NCH_3)_2Cl_6$ .

Analysis of  $P_2(NCH_3)_2O_2Cl_2$  (222.9)

calc:	12.57 N	27.79 P	31.81 Cl	10.77 C	2.71 H
found:	12.49 N	27.40 P	31.83 Cl	10.72 C	2.70 H

Molecular weight (ebullioscopically in benzene and dichloroethane):  $222 \pm 1.5$  (mean from 6 determinations).

## C. 2, 4-DITHIO-2, 4-DICHLORO-1, 3-DIMETHYLCYCLODIPHOSPHAZANE (VIII)

A total of 103 g of dry pyridine was added to a solution of 100 g of V (0.3 mole) in 1 liter of dry benzene. Dry  $H_2S$  was passed into the stirred solution at room temperature. After a short time, a precipitate of pyridinium chloride appeared, which was formed in an approximately theoretical amount in the course of 15 hours. The precipitate was then filtered off and washed repeatedly with benzene. The filtrate was subsequently evaporated in aspirator vacuum, care being taken to exclude moisture throughout each phase of the operations. A yellowish crystalline residue was obtained following removal of the solvent; this product can be recrystallized from cyclohexane or (preferably) from petroleum ether. Purification can also be achieved by sublimation at  $70^{\circ}/0.1$  mm Hg. Melting point:  $120^{\circ}$  to  $122^{\circ}$  (unsharp). Yield: 60 g (78.3% of theory).

Analysis of  $P_2S_2(NCH_3)_2Cl_2$  (255.1)

calc:	24.29 P	10.98 N	25.14 S	27.80 Cl
found:	24.14 P	10.77 N	24.75 S	27.50 Cl

Molecular weight (ebullioscopically in benzene and dichloroethane):  $256 \pm 0.5$  (mean for 7 determinations).

## D. 2, 4-DITHIO-2, 4-DIANILINO-1, 3-DIMETHYLCYCLODIPHOSPHAZANE (IX)

A total of 37 g of aniline was added dropwise with stirring in the course of 20 min to a solution of 25.5 g  $P_2(NCH_3)_2S_2Cl_2$  (VIII) in 800 ml of dry benzene. The reaction mixture was allowed to stand under continuous stirring for 24 hours, after which it was heated to boiling for a short time and filtered while still hot through a frit to separate the anilinium chloride formed in the reaction. The solvent was removed in aspirator vacuum, leaving a colorless crystalline residue. When this was dissolved in 600 ml of hot carbon tetrachloride and the solution allowed to cool, star-shaped crystals separated. These were recrystallized in the same way. Yield: 8 g (25% of theory). The substance melted at  $146^{\circ}$  and was readily soluble in dichloroethane, benzene, and  $CCl_4$ . It is not hygroscopic, although it is slowly darkened by the action of light.

Analysis of  $P_2(NCH_3)_2S_2(NHC_6H_5)_2$  (368.4)

calc:	15.21 N	16.81 P	17.40 S	45.64 C	4.92 H
found:	14.96 N	17.00 P	17.37 S	45.66 C	4.88 H

Molecular weight (ebullioscopically in benzene): 368 (mean from 3 determinations).

## Part II

## E. 2, 4-DITHIO-2, 4-BIS-DIETHYLAMINO-1, 3-DIMETHYLCYCLOPHOSPHAZANE (X)

A solution of 6 g diethylamine in 100 ml of benzene was dropped in the course of 20 min with stirring into a solution of 13 g of  $P_2(NCH_3)_2S_2Cl_2$  in 350 ml of dry benzene at room temperature. The reaction was mildly exothermic and a white precipitate was formed, which was filtered off on a frit after two hours. The filtrate was concentrated to 50 ml in aspirator vacuum and allowed to cool, whereupon crystals separated. These were recrystallized from 700 ml of cyclohexane. The substance melts at  $169^\circ$  and is not hygroscopic. Yield: 12 g (75% of theory).

Analysis of  $P_2(NCH_3)_2S_2[N(C_2H_5)_2]_2$  (328.4)

calc:	17.06 N	18.86 P	19.53 S	36.57 C	7.98 H
found:	16.77 N	19.20 P	19.78 S	37.01 C	8.04 H

Molecular weight (ebullioscopically in benzene): 328 (graphic mean from 3 determinations).

## F. N-METHYLIMIDODITHIOPHOSPHORIC TETRA-N-METHYLAMIDE (XI)

A total of 13.4 g of VIII was added in one portion to 100 ml of methylamine which had been condensed at  $-50^\circ$  under exclusion of moisture. The clear solution which resulted was allowed to stand at room temperature until most of the excess methylamine had evaporated and then residual amine was pumped off in vacuum. The white solid which remained was boiled with several separate portions of benzene, care being taken to apply heat for only a short time in order to avoid loss of amine by chemical fission. The benzene solutions were subsequently concentrated in vacuum, whereupon the product crystallized out on cooling. Purification was accomplished by recrystallization from carbon tetrachloride or methylene chloride. Yield: 12.5 g (86.4% of theory). Melting point:  $92^\circ$ .

Analysis of  $P_2S_2(NCH_3)(NHCH_3)_4$  (275.3)

calc:	22.50 P	25.44 N	23.29 S
found:	22.70 P	25.22 N	23.64 S

Molecular weight (ebullioscopically in benzene):  $278 \pm 6$  (mean from 4 determinations).

## G. 2, 4-DITHIO-2, 4-BIS-N-METHYLAMINO-1, 3-DIMETHYLCYCLODIPHOSPHAZANE (XII)

Sublimation of XI at  $180^\circ$  to  $200^\circ/15$  mm Hg led to XII in ca 80 percent yield. The product was recrystallized from dichloroethane or acetonitrile. Melting point:  $224^\circ$ .

Analysis of  $P_2S_2(NCH_3)_2(NHCH_3)_2$  (244.3)

calc:	25.37 P	22.94 N	26.25 S
found:	25.36 P	23.04 N	26.50 S

Molecular weight (ebullioscopically in acetone):  $243 \pm 2$  (mean from 4 determinations).

H.  $P_4(NCH_3)_6Cl_8$  (XXII)

A mixture of 208.5 g  $PCl_5$  and 75 g of methylammonium chloride (not previously dried) was placed in 750 ml of tetrachloroethane and heated to boiling. The evolution of HCl ceased after about 6 hours. The reaction mixture was cooled to  $0^\circ$  and the crystallized product (V) filtered.

## Part II

The filtrate was evaporated in aspirator vacuum in a thin-layer evaporator to about half the original amount and then cooled to 0°C. This procedure led to a further quantity of V. Next, tetrachloroethane was evaporated off in the same way and the residue warmed with 200 ml of carbon tetrachloride. In the absence of residual tetrachloroethane, this treatment permits removal of remaining traces of V and oily by-products from the finely crystalline crude product. The latter consists of a white material corresponding to XXII. The yield is variable, amounting to about 3 g (ca 2% of theory). XXII can be recrystallized from benzene. In a sealed tube, the substance melts with decomposition at 395°.

Analysis of  $P_4(NCH_3)_6Cl_8$  (581.8)

calc: 21.30 P 14.45 N 48.75 Cl 12.38 C 3.12 H  
found: 21.24 P 14.36 N 47.63 Cl 12.9 C 3.29 H

Molecular weight (ebullioscopically in benzene and in dichloroethane): 584±16 (mean from 6 determinations).

I.  $P_4(NCH_3)_6O_2Cl_4$  (XXIV)

A total of 5.8 g of XXII was dissolved to the limit of solubility in 400 ml of dry benzene. Dry  $SO_2$  was sparged into the stirred mixture at room temperature for 2 to 3 hours. The resulting clear solution was then evaporated to dryness in an aspirator vacuum. The white solid residue was recrystallized twice from 50 ml of benzene and dried in vacuo. Yield: 3 g (65% of theory). The substance is hygroscopic; meltingpoint: 185° to 220° with decomposition. XXIV is readily soluble in pyridine, methylene chloride, dichloroethane, and benzene.

Analysis of  $P_4(NCH_3)_6O_2Cl_4$  (471.98)

calc: 17.80 N 26.25 P 30.05 Cl 15.27 C 3.34 H  
found: 17.23 N 26.77 P 29.63 Cl 15.66 C 3.81 H

J.  $P_4(NCH_3)_6S_2Cl_4$  (XXIII)

A total of 11.6 g of XXII was suspended in 800 ml of dry benzene. After the addition of 13 g of dry pyridine, dried  $H_2S$  was passed into the stirred mixture for 12 hours. The solution turned yellow and pyridinium chloride was precipitated; this was subsequently filtered off on a frit, care being taken to exclude moisture. The filtrate was evaporated to dryness in vacuum, leaving a yellowish solid residue. This crude product was recrystallized first from 200 ml of benzene and then from cyclohexane. Yield: 6 g (60% of theory). The compound melts at 230° with decomposition; it dissolves readily in benzene, tetrachloroethane, and dichloroethane and less easily in cyclohexane.  $P_4(NCH_3)_6S_2Cl_4$  is somewhat hygroscopic.

Analysis of  $P_4(NCH_3)_6S_2Cl_4$  (504.12)

calc: 24.58 P 16.67 N 12.72 S 28.13 Cl 14.29 C 3.5 H  
found: 24.79 P 16.62 N 12.79 S 28.26 Cl 14.64 C 3.5 H

Molecular weight (ebullioscopically from dichloroethane): 497 (mean from 3 determinations).

## Infrared Spectra (in KBr)

$P_4(NCH_3)_6Cl_8$ : 2960s, 2820vw, 1460m, 1425m, 1285sh, 1202s, 1173m, 1077w, 1018w, 922w, 877s, 843vs, 793w, 715vs, and 654m ( $cm^{-1}$ )

Part II

$P_4(NCH_3)_6S_2Cl_4$ : 2900s, 1460s, 1425w, 1378m, 1278vw, 1200s, 1156s, 890m, 845vs, br,  
787m, 758m, 730s, and 684s ( $cm^{-1}$ )

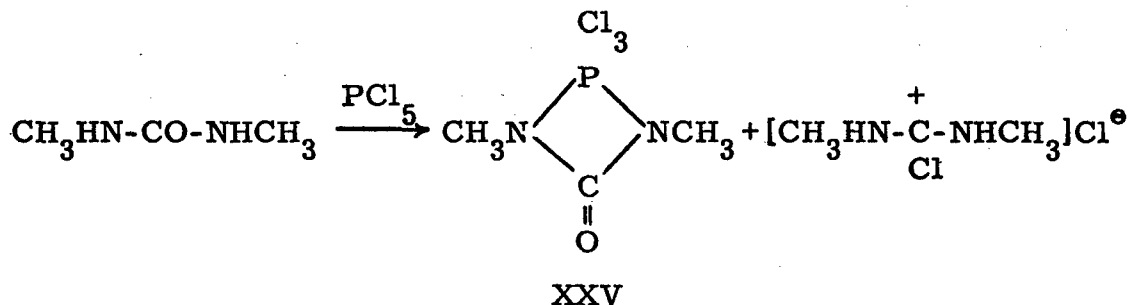
$P_4(NCH_3)_6O_2Cl_4$ : 2950s, 1465s, 1315m, 1251m, 1210m, 872s, 832s, 793m, 696m, and  
.680m ( $cm^{-1}$ )



### SECTION III

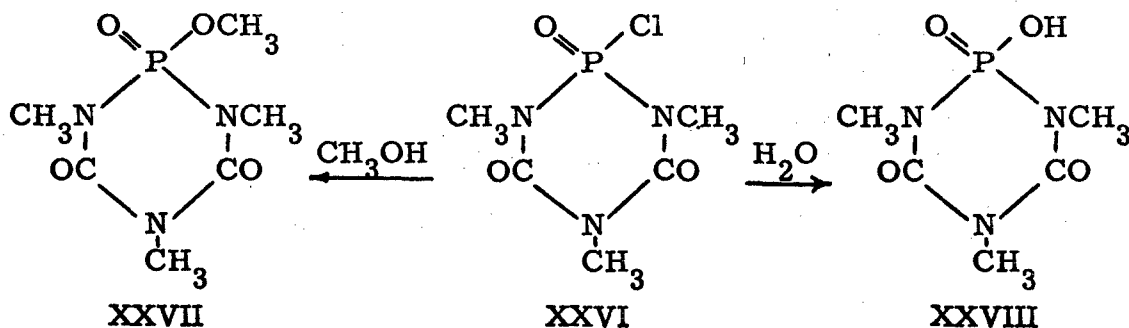
#### COMPOUNDS WITH FOUR-MEMBERED RING SYSTEMS CONTAINING P, N AND C

We investigated the reaction between N, N'-dimethyl urea and phosphorus pentachloride. When these reagents were reacted in dry carbon tetrachloride, HCl was evolved and a compound was formed to which formula XXV can be ascribed (Reference 12).



This compound is obtained when the oily crude product which initially separates (yield: 90%) is distilled in vacuo. The distillation residue is a solid from which a second phosphorus compound with the composition  $\text{C}_5\text{H}_9\text{ClN}_3\text{O}_3\text{P}$  can be isolated by sublimation in vacuo at  $80^\circ$  to  $100^\circ$ . This same product was also obtained when compound XXV was heated in a sublimation apparatus for several days at  $160^\circ$  to  $180^\circ$  at a pressure of 0.01 mm Hg.

Under these conditions, XXV decomposes; the cold trap in the vacuum line afterwards contained a material which was identified as phosphorus oxytrichloride.  $\text{C}_5\text{H}_9\text{ClN}_3\text{O}_3\text{P}$  was collected on the cold finger. The sublimation residue consisted of a yellow-brown frothy solid. It proved possible to determine the constitution of  $\text{C}_5\text{H}_9\text{ClN}_3\text{O}_3\text{P}$ , for which formula XXVI was established. The substance is colorless and crystalline; it dissolves in benzene and in other organic solvents but is insoluble in petroleum ether. The action of water causes evolution of hydrogen chloride. When the latter is removed in vacuum, a colorless oil is produced which solidifies to fully transparent crystals. Formula XXVIII was ascribed to this material. Corresponding treatment with methyl alcohol leads to the colorless crystalline compound XXVII.



The polymer which is formed together with XXVI in the thermal decomposition of XXV is insoluble in all common organic solvents. However, this polymer reacts with water and alcohols to furnish new polymeric products which are soluble.

## Part II

The polymer  $P_1$  produced in the thermal decomposition of XXV has the following composition: 20.28% C; 2.87% H; 15.68% N; 16.7% P; 26.5% Cl; 17.5% O.

Decomposition occurs when  $P_1$  is heated first to 150° and then gradually to 400°. A solid product is thereby formed which is stable between 400° and 520°, first decomposing above 600°.

When heated in an open flame, the substance becomes black but does not burn. At red heat, OPN is produced which does not undergo further combustion.

When subjected to the action of boiling methanol for several hours, polymer  $P_1$  gives rise to a viscous, sticky paste which is soluble in alcohols and whose solution can be readily applied to a large variety of surfaces, e.g., wood or cloth. The paste itself can also be directly applied. The paste (designated as  $P_2$ ) has the following composition: 19.7% C; 5.9% H; 17.2% N; 12.3% P; 13.3% Cl; leaving 32.5% which presumably consists of oxygen.

$P_2$  decomposes at temperatures between 230° and 400°. The first product of decomposition is stable up to 540°, above which it too decomposes.

$P_1$  is completely dissolved by the action of boiling water. When the excess of water is removed in vacuum, a transparent film is obtained which is stable up to 250°. This film (designated as  $P_3$ ) has the composition 17.2% C; 5.05% H; 21.9% N; 13.4% P; 11.7% Cl; remainder (presumably O): 30.8%.

It is not yet possible to establish structural formulae for these polymeric products of pyrolysis of substance XXV. Nonetheless, experimental results indicate that pyrolysis of the four-membered ring system XXV provides a pathway to an interesting group of polymers which have the advantage of being convertible into alcohol-soluble and even water-soluble materials.

#### A. PREPARATION OF COMPOUND XXV

A solution of 88 g (1 mole) NN'-Dimethylurea in 1750 ml  $CCl_4$  was placed in a 2-1 round-bottomed, three-necked flask, fitted with a reflux-condenser, a  $CaCl_2$ -drying-tube and a mechanical stirrer. To this well-stirred and cooled mixture was added 220 g (about 1.1 mole) phosphorus pentachloride. The rate of addition was so adjusted that the temperature of the solution did not rise over 70°. After thirty minutes of gently refluxing, the mixture was cooled in order to crystallize the greenish oil on the surface  $[(CH_3-NH)_2CCl_2]$ , the liquid was separated and the solvent removed.

The high vacuum distillation was done in two or three portions for better yield (polymers). The product was a colorless liquid and very hygroscopic.

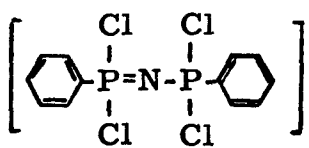
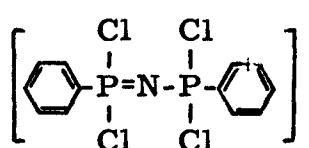
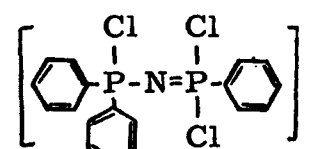
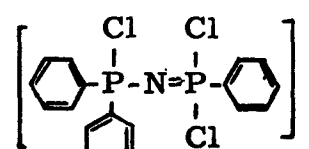
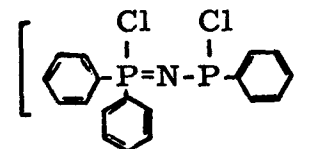
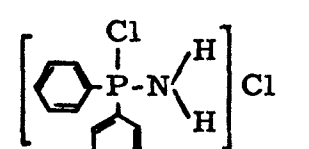
bp 55°/1 mm Hg; yield: 76 g = 34%; chem shift  $P^{31}$  NMR +60 ppm (related to 85%  $H_3PO_4$ ).

## SECTION IV

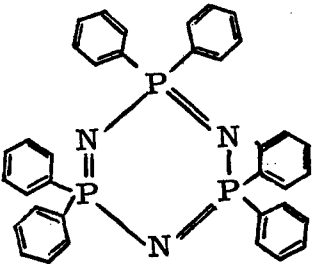
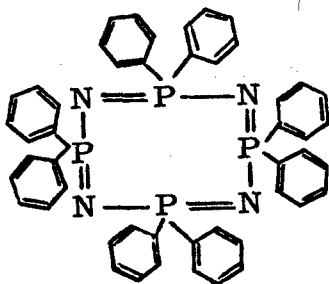
## COMPOUNDS WITH P-N-P-CHAINS

According to the research proposal the preparation of the following phosphorus nitride salts was realized. The structures were established.

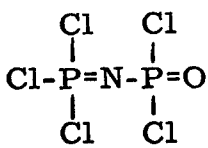
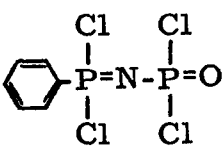
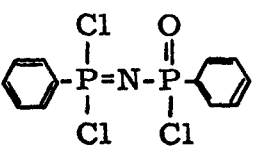
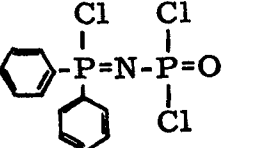
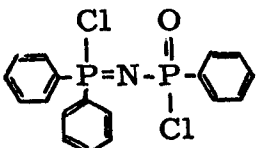
Substance	mp/bp	nmr $P^{31}$ $\delta$
XXIX $\left[ \begin{array}{cc} \text{Cl} & \text{Cl} \\   &   \\ \text{Cl}-\text{P}=\text{N}-\text{P}-\text{Cl} \\   &   \\ \text{Cl} & \text{Cl} \end{array} \right] \text{PCl}_6$	solid with water fast hydrolysis	$\delta = -21.4, +300$
XXX $\left[ \begin{array}{cc} \text{Cl} & \text{Cl} \\   &   \\ \text{Cl}-\text{P}=\text{N}-\text{P}-\text{Cl} \\   &   \\ \text{Cl} & \text{Cl} \end{array} \right] \text{Cl}$	solid with water fast hydrolysis	$\delta = -21.4$
XXXI $\left[ \begin{array}{cc} \text{Cl} & \text{Cl} \\   &   \\ \text{C}_6\text{H}_5-\text{P}=\text{N}-\text{P}-\text{Cl} \\   &   \\ \text{Cl} & \text{Cl} \end{array} \right] \text{PCl}_6$	solid mp $124^\circ$	$\delta = -41, 8, -24, 7, +300$
XXXII $\left[ \begin{array}{cc} \text{Cl} & \text{Cl} \\   &   \\ \text{C}_6\text{H}_5-\text{P}-\text{N}=\text{P}-\text{Cl} \\   &   \\ \text{C}_6\text{H}_5 & \text{Cl} \end{array} \right] \text{PCl}_6$	solid mp $163^\circ-166^\circ$	$\delta = -42, 3, -14, 3, +300$
XXXIII $\left[ \begin{array}{cc} \text{Cl} & \text{Cl} \\   &   \\ \text{C}_6\text{H}_5-\text{P}-\text{N}=\text{P}-\text{Cl} \\   &   \\ \text{C}_6\text{H}_5 & \text{Cl} \end{array} \right] \text{Cl}$	solid	$\delta = -42, 3, -14, 3$

	Substance	mp/bp	nmr $P^{31}$ $\delta$
XXXIV	 $PCl_6$	solid mp 132°	$\delta = -41, 7, +300$
XXXV	 $Cl$	solid mp 210°	$\delta = -41, 7$
XXXVI	 $Cl$	solid but not crystalline	$\delta = -46, 4, -38, 1$
XXXVII	 $PCl_6$	solid	$\delta = -46, 4, -38, 1, +300$
XXXVIII	 $Cl$	solid pyrolysis yields 3, A and 3, B hydrolysis yields IL	$\delta = -43, 3$
XXXIX	 $Cl$	solid when heated to 270°, 3, A and 3, B are formed	$\delta = -51, 0$

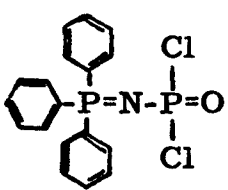
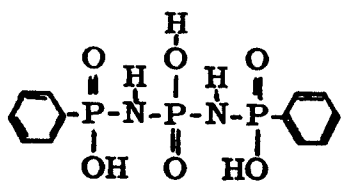
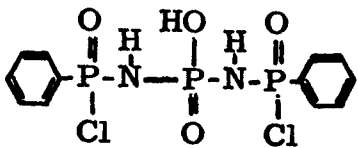
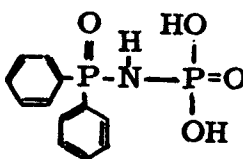
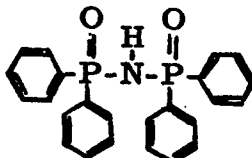
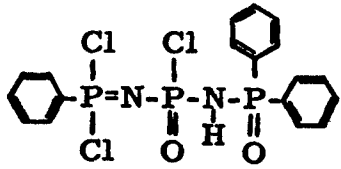
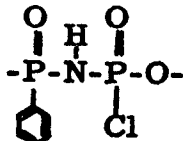
## Part II

Substance	mp/bp	nmr $P^{31}$ $\delta$
 3, A		
 3, B		

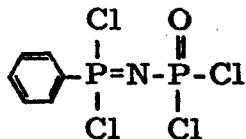
The following oxygen containing compounds were obtained.

XL		mp +35, 7 bp <sub>1</sub> 102° n <sub>D</sub> <sup>25</sup> 1.5305	$\delta = +0, 1, +14, 2$
XLII		bp 0.001 148°-150° n <sub>D</sub> <sup>22</sup> 1.5838 pyrolysis yields longer chains	$\delta = -20, 0, +8, 4$
XLIII		liquid bp 0.01 210°	$\delta = -14, 9, -11, 9$
XLIV		liquid bp 0.01 205°-215° pyrolysis yields B hydrolysis yields XX	$\delta = -29, 0, +8, 7$
XLV		solid but not crystalline	$\delta = -31, 4, -18, 4$

## Part II

	Substance	mp/bp	nmr $P^{31}$ $\delta$
XLV			$\delta = -12, 9, +9, 6$
XLVI		solid	
XLVII		solid	
XLVIII		solid mp 201°	
XLIX		solid mp 171°	
L		solid	
LI		solid	

The polymeric compound LI was built from compound XLII.



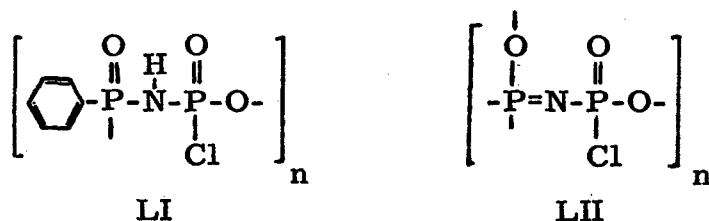
XLII

This substance was heated at 90° to 100° in a distillation apparatus which was directly connected with a high vacuum pump, whereby distilled water was simultaneously introduced very slowly directly into the hot oily liquid. Under these conditions reaction occurred with the evolution of hydrogen chloride. The HCl and water vapor were condensed in a trap cooled with liquid nitrogen. When this procedure was maintained for 20 to 30 minutes while the bath temperature was raised slowly from 150° to 200°, the walls of the flask gradually became covered with small bubbles and the originally dark brown oil swelled to a greyish froth.

The polymeric product thus formed was isolated by allowing the flask to cool, bringing the system to atmospheric pressure, and pulverizing the brittle, spongy mass under petroleum ether. The polymer is hygroscopic; it swells in contact with most organic solvents such as acetone, benzene, methylene chloride, chloroform, carbon tetrachloride, etc. The polymer does not dissolve in boiling water although it does interact under these conditions, as is evidenced by a decrease in the chlorine content. A consistent analysis of the polymer was very difficult to obtain, because the composition varied considerably according to the conditions of the synthesis. If the temperature is too low, viscous, greyish-brown products result in place of the hard, froth-like substance capable of swelling. However, if the procedure described above is followed exactly, the results of analysis agree with the formula  $\text{C}_6\text{H}_6\text{ClNP}_2\text{O}_3$  and it can be concluded that the polymer must be of type LI.

Thermogravimetric studies of substance LI revealed that initial decomposition occurs at 340° to 400° followed by a second stage of decomposition at 540° to 690°. In the temperature range corresponding to the first decomposition, the loss in weight amounted to 33.6 percent. This can be interpreted by loss of the phenyl group. The resulting polymer, which is stable up to 540°, is then apparently of type LII.

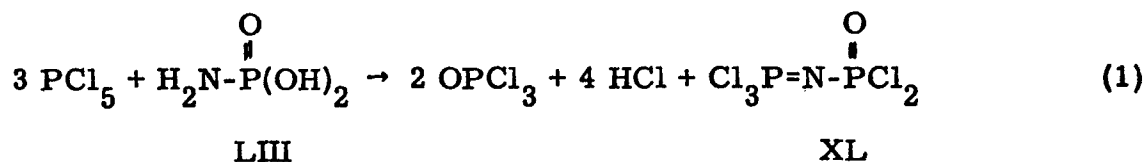
Thus, polymer LII originates from a substance capable of swelling and which in this form can be applied to the surfaces of wood and cloth, etc. This procedure is therefore a means of preparing a useful fireproofing material.



In this way we were able to obtain a new type of polymer which appears particularly promising because the compound still contains a chlorine atom; this halogen can very probably be substituted with the result that the solubility and other desirable qualities of the products should be enhanced.

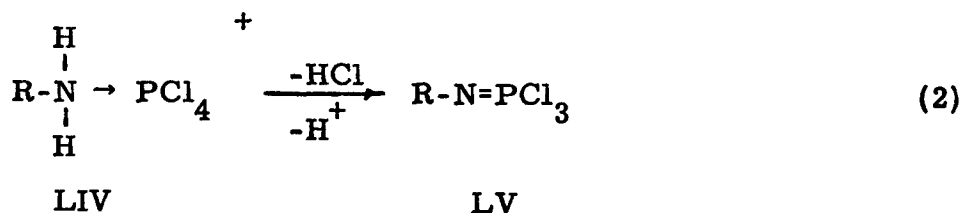
The formation of compound XL is interesting and shows characteristic aspects to the whole class of compounds.

The reaction of amides of orthophosphoric acid and of thiophosphoric acid with  $\text{PCl}_5$  has been investigated by Becke-Goehring et al. (Reference 13). It was shown that orthophosphoric acid monoamide LIII reacts readily with  $\text{PCl}_5$  according to Equation (1).



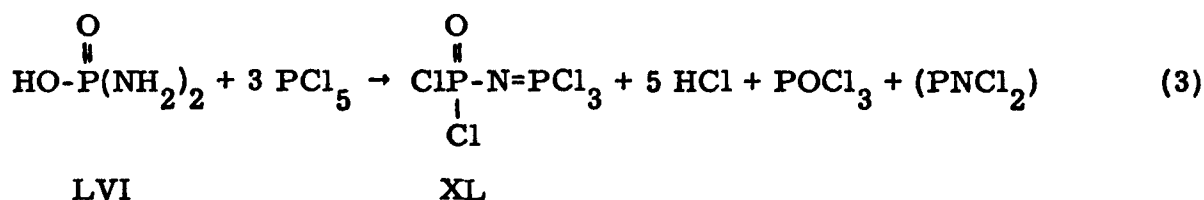
This reaction led to the formation of compound XL which is also obtained by the action of  $\text{PCl}_3$  upon  $\text{N}_2\text{O}_4$  (Reference 14) as well as in the reaction of hydroxylammonium salts with phosphorus pentachloride (Reference 15).

The formation of XL according to Equation (1) represents a type of reaction which was first observed by Kirsanov in studies dealing with sulfuric acid amides (Reference 16). According to this scheme, the reaction of an acid amide with  $\text{PCl}_5$  involves primary dissociation of  $\text{PCl}_5$  into  $[\text{PCl}_4]^+$  and  $[\text{PCl}_6]^-$  (Reference 17). Nucleophilic attack by the nitrogen of the acid amide upon the  $\text{PCl}_4$  cation then leads to the intermediate product LIV, which splits off  $\text{HCl}$  to form a trichlorophosphazo compound LV, (Reference 18).



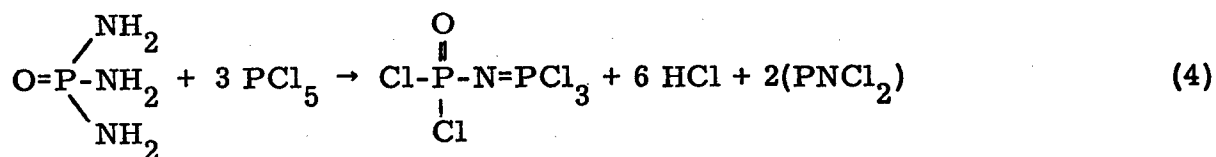
$\text{PCl}_5$  reacts with LIII not only in the sense of a Kirsanov reaction; it reacts simultaneously in the usual manner with the hydroxyl groups present, causing them to be replaced by  $\text{Cl}$ .

Compound XL is also obtained when  $\text{PCl}_5$  is reacted with orthophosphoric acid diamide LVI in place of LIII, but the yield is only about 50 percent according to Equation (3).

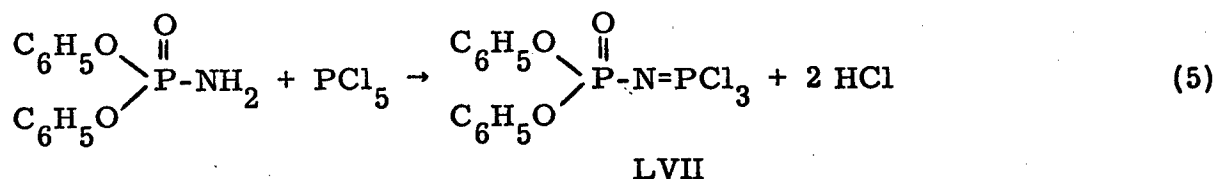


This reaction with  $\text{PCl}_5$  proceeds in the sense of a Kirsanov reaction and in addition replacement of a hydroxyl and an amido group by  $\text{Cl}$  occurs. Orthophosphoric acid triamide behaves analogously.

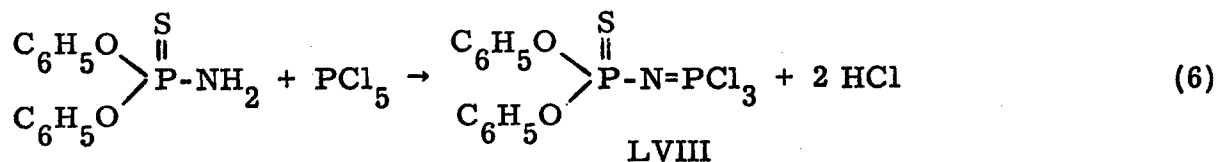




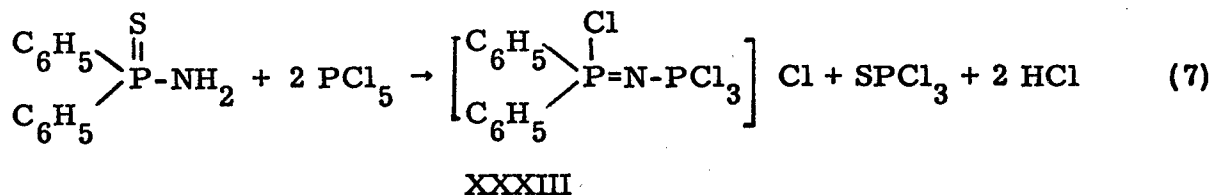
A. V. Kirsanov was able to show that substituted phosphoric acid amides can also react with  $\text{PCl}_5$  according to Equation (2) (Reference 19); he obtained compound LVII when orthophosphoric acid amide diphenyl ester was reacted with  $\text{PCl}_5$ .



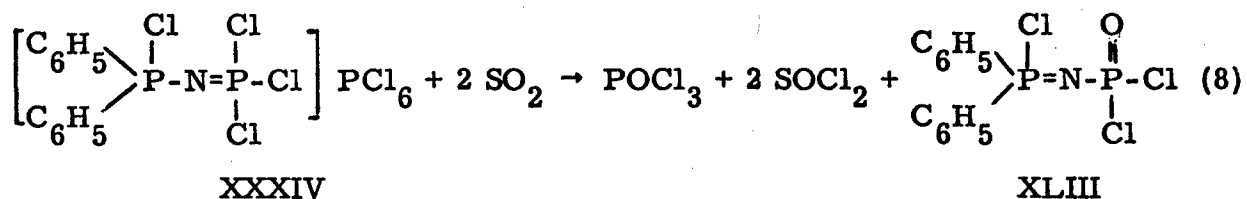
Kirsanov also prepared the corresponding thiophosphoryl compound(LVIII) in a similar manner (Reference 19).



An analogous reaction occurs when diphenylthiophosphinic amide is introduced in place of thiophosphoric ester amide, but in addition, further  $\text{PCl}_5$  causes substitution of the sulfur and formation of the phosphorus nitride salt XXXIII.

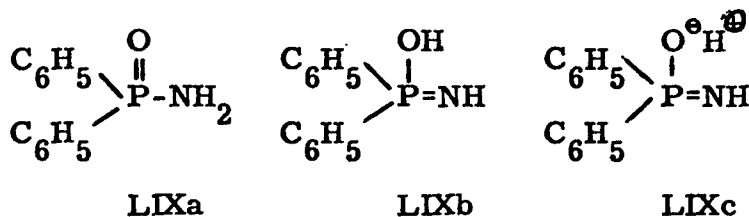


With more  $\text{PCl}_5$  compound XXXII is formed. The reaction of XXXII with  $\text{SO}_2$  proceeds according to Equation (8).

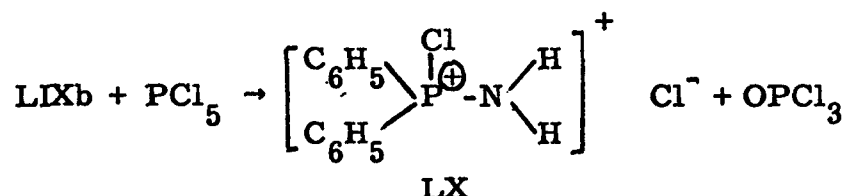


Compound XLIII was formed which is a liquid (bp  $210^\circ/0$ , 01 mm Hg). Careful hydrolysis of XIV leads to compound LXIII, a colorless crystalline substance (mp  $201^\circ-203^\circ$ ). It is possible that the high melting point of compound LXIII is due to hydrogen bonding.

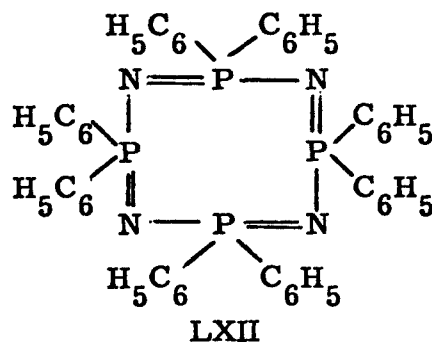
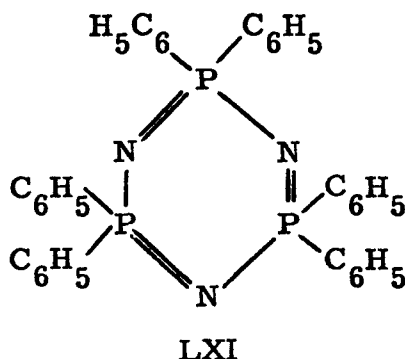
It was found that diphenylphosphinic amide LIX reacts with  $\text{PCl}_5$  in a manner entirely different from that of the phosphoric and thiophosphoric derivatives already studied. Diphenylphosphinic amide apparently exists in the tautomeric forms LIXa and LIXb.



LIXb and LIXc are chlorinated very readily by  $\text{PCl}_5$ , furnishing chlorodiphenylphosphine imine hydrochloride (III) (Equation 6).



LX is a colorless, crystalline solid which evolves  $\text{HCl}$  even at temperatures below  $100^\circ$ ; when heated slowly to  $270^\circ$  to  $280^\circ$  under slightly reduced pressure, the substance decomposes to give hexaphenyl tris(phosphorus nitride) (LXI) in 51 percent yield and octaphenyl tetrakis(phosphorus nitride) (LXII) in ca 30 percent yield.



LX hydrolyzes with evolution of  $\text{NH}_3$  when treated with warm 2 M  $\text{KOH}$  solution; acidification with  $\text{HCl}$  causes precipitation of diphenylphosphinic acid (mp  $190^\circ$ ).

The  $\text{P}^{31}$  NMR spectrum of a solution of LX in methanol showed a chemical shift of  $\delta = -51$ , 0 ppm, referred to 85 percent  $\text{H}_3\text{PO}_4$ . This indicates that the extent of electronic shielding of the phosphorus atom in this compound is small and that the positive ionic charge is to be ascribed to the phosphorus and not to the nitrogen atom. The infrared spectrum of III closely resembles that of triphenylphosphine imine hydrochloride with the exception that an additional band is present at  $1400 \text{ cm}^{-1}$  in the former case.

## Part II

A.  $[(C_6H_5)_2P(Cl)-NH_2]Cl$  (LX)

Thirty-three g (0.153 mole) of  $(C_6H_5)_2P(O)NH_2$  were dissolved in 400 ml of chloroform in a two-necked flask fitted with a stirrer and a drying tube; 32 g (0.153 mole) of  $PCl_5$  were added with stirring, whereupon remaining traces of amide dissolved immediately. Within half a minute following the addition of the  $PCl_5$ , the solution became noticeably warm; cooling was then applied with an ice water bath and stirring continued for two minutes. At the end of this time stirring was stopped and the cooling bath removed, after which 400 ml of  $CCl_4$  were dropped into the reaction mixture in the course of two hours. It is expedient to let the  $CCl_4$  run in along the side of the flask, as this enhances crystallization of the product. LX then separates in the form of colorless needles; these were subsequently filtered off on a frit and washed with  $CCl_4$  and petroleum ether. Attempts to dry the compound in vacuo lead to a loss of from 2 to 4 percent HCl. Yield: 80 percent of theory.

B. PREPARATION OF  $[(C_6H_5)_2P(Cl)=N-PCl_3]PCl_6$  (XXXII)

A solution of 14.4 g (0.062 mole) of  $(C_6H_5)_2P(S)NH_2$  in 200 ml of dry chloroform was placed in a flask provided with a stirrer and a reflux condenser fitted with a drying tube; 40 g (0.19 mole) of  $PCl_5$  were added with stirring and the mixture was heated slowly to 50° to 60°. After the vigorous evolution of HCl had subsided (1/2-1 hour), the mixture was boiled under reflux for a further two hours. Most of the solvent was then distilled off, and the cooled oily residue treated with dry benzene. This first benzene extract was poured off and the residue shaken again twice with fresh portions of benzene. After the third wash, the reaction product separated into pale greenish-yellow crystals. The yield of the already very pure crude product is 90 to 100 percent; the substance can be recrystallized from small amounts of chloroform (100 ml).

Analysis of X:  $C_{12}H_{10}Cl_{10}NP_3$  (615.72)

calc: 23.41 C 1.64 H 57.58 Cl 2.28 N 15.09 P

found: 24.65 C 2.18 H 57.5 Cl 2.28 N 14.6 P

This substance is very hygroscopic and can be handled only in an absolutely dry atmosphere. It is difficultly soluble in nonpolar solvents such as benzene, carbon tetrachloride, and petroleum ether and soluble in tetrachloroethane, chloroform, and phosphorus oxychloride. X melts at 163° to 166°. The molecular weight measured in nitrobenzene is 285 (calc 615.72), since the salt dissociates in this solvent. The assumption that dissociation into two univalent ions occurs was confirmed by measurement of the equivalent conductivity in nitrobenzene ( $\chi = 0.5 \cdot 10^{-7} \Omega^{-1} \text{cm}^{-1}$ ).  $\Lambda_c(20^\circ) = 21 \Omega^{-1} \text{cm}^{-1} \text{mole}^{-1}$  ( $c = 0.8 \cdot 10^{-2} \text{mole/e}$ ).

C. PREPARATION OF  $[(C_6H_5)_2P(Cl)=N-PCl_3]Cl$  (XXXIII)

The chloride XXXIII is obtained in the same way as XXXII when a mole ratio of  $(C_6H_5)_2P(S)NH_2:PCl_5$  of 1:2 is employed. After washing with benzene, XXXIII remains as an oil. The product crystallizes when the remaining traces of solvent are pumped off in vacuo.

D. PREPARATION OF  $(C_6H_5)_2P(Cl)=N-P(O)Cl_2$  (XLIII)

Dry  $SO_2$  was passed into  $[(C_6H_5)_2P(Cl)=N-PCl_3]PCl_6$  in a flask fitted with a gas inlet and a gas outlet tube. The crystalline mass liquefied; after the mixture had become homogeneous,  $SO_2$  was passed in for a further hour.  $SO_2$ ,  $SOCl_2$  and  $OPCl_3$  were then removed in an aspirator vacuum. The residue was distilled rapidly in vacuo at  $205^\circ$  to  $215^\circ/0.01$  mm Hg, care being taken to select a short distillation path. Yield: 90 percent of theory.

Analysis of XLIII:  $C_{12}H_{10}Cl_3NOP_2$  (352.54)

calc:	40.88 C	2.86 H	30.17 Cl	3.97 N	4.54 O	17.57 P
found:	40.81 C	2.91 H	30.22 Cl	3.98 N	-- O	17.92 P

The cryoscopically determined molecular weight in benzene was 368 (calc 352.5). The compound is a pale yellow, oily liquid. It is considerably less sensitive towards hydrolysis than the salt and is soluble in benzene, dioxan, and carbon tetrachloride.

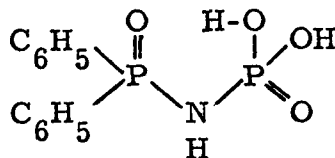
E. PREPARATION OF  $(C_6H_5)_2P(O)-NH-P(O)(OH)_2$ 

$(C_6H_5)_2P(Cl)=N-P(O)Cl_2$  was diluted with twice its quantity of dioxan and this mixture treated in turn with twice its amount of water. The mixture was shaken and kept at room temperature. The acid separated slowly as a white solid. This material was then washed thoroughly with water and recrystallized from ethanol. When well dried, the white needles melted at  $201^\circ$  to  $203^\circ$ .

Analysis of XV:  $C_{12}H_{13}NO_4P_2$  (297.19)

calc:	48.49 C	4.41 H	4.71 N	21.53 O	20.86 P
found:	48.44 C	4.58 H	4.80 N		20.77 P

Titration gave an equivalent weight of 296 with methyl orange as indicator and 147 with phenolphthalein. This is in agreement with the calculated molecular weight of 297.2 and the formula LXIII.



LXIII

F.  $[(C_6H_5)_2PN]_3$  (LXI) AND  $[(C_6H_5)_2PN]_4$  (LXII)

A sample, 8.5 g, of phosphine imine hydrochloride (LX) was heated slowly to  $275^\circ$ . This temperature was maintained for two hours and the  $HCl$  formed pumped off under partial vacuum. The melt solidified to a brittle, greyish mass which was subsequently extracted with 200 ml of benzene in a Soxhlet apparatus. Progressive removal of the benzene in vacuum lead to crystallization first of LXI (3.1 g, 51% of theory) and then of LXII (1.8 g, 30% of theory).

Part II

Analysis of LXI:  $C_{36}H_{30}N_3P_3$  (597.59)

calc:	72.36 C	5.06 H	7.03 N	15.55 P
found:	72.38 C	5.14 H	7.05 N	15.76 P

Molecular weight (ebullioscopically in benzene): 571; mp 223° to 227°,  $P^{31}$  NMR spectrum (benzene): maximum at -14.2 ppm (referred to 85%  $H_3PO_4$ ), (Reference 5).

Analysis of LXII:  $C_{48}H_{40}N_4P_4$  (796.78)

calc:	72.36 C	5.06 H	7.03 N	15.55 P
found:	72.66 C	4.73 H	6.91 N	15.37 P

Molecular weight (ebullioscopically in benzene): 843; mp 315° to 318°

G. INFRARED SPECTRA

For  $[(C_6H_5)_2P(Cl)NH_2]Cl$  (LX): 3170s, 3060s, 1590w, 1560w, 1480w, 1440s, 1400s, 1130s, 1028s, 947s, 750s, 730s, 690s ( $cm^{-1}$ )

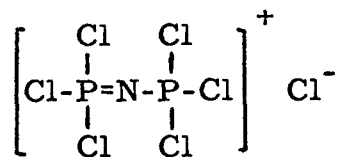
For  $[(C_6H_5)_3PNH_2]Cl$ : 3090s, 3000s, 1595w, 1560w, 1495w, 1450s, 1130s, 1000s, 970s, 760s, 725s, 695s ( $cm^{-1}$ )

## SECTION V

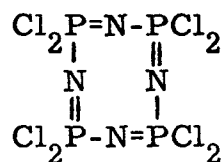
PHOSPHONITRILIC CHLORIDES  $(\text{NPCl}_2)_n$  AND DERIVATIVES

According to the research proposal we had to study new and efficient methods for preparing phosphorus nitride chlorides containing P-N ring systems. We used the compound  $\text{NP}_2\text{Cl}_7$  as starting material.

$\text{NP}_2\text{Cl}_7$  is prepared by the reactions of  $[\text{NH}_3\text{OH}]\text{Cl}$  with  $\text{PCl}_5$  or via  $\text{PCl}_5 + \text{NH}_4\text{Cl}$  (Reference 20). The structure is shown by formula XXX.

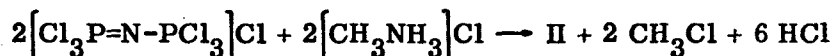


XXX

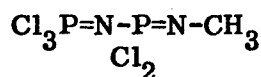


LXVI

It was suspended in *s*-tetrachloroethane and mixed with an excess of  $[\text{CH}_3\text{NH}_3]\text{Cl}$ . At a reaction temperature of  $110^\circ$  to  $120^\circ$  the following reaction was observed.

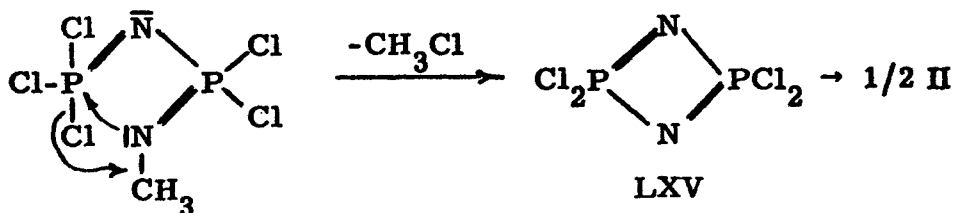


The first reaction product was compound LXIV.



LXIV

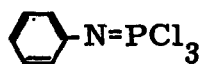
But LXIV is not stable. When heated,  $\text{CH}_3\text{Cl}$  is released and LXV is formed. However, LXV dimerizes immediately.



Thus a good method was obtained for the preparation of tetrameric phosphorus nitride chloride LXVI. The yield of  $[\text{NPCl}_2]_n$  was nearly quantitative. A large amount of  $[\text{NPCl}_2]_4$  was obtained;  $[\text{NPCl}_2]_n$  formed, however, contained approximately 15 percent of  $[\text{NPCl}_2]_3$ . The amount of  $[\text{NPCl}_2]_5$ ,  $[\text{NPCl}_2]_6$ ,  $[\text{NPCl}_2]_7$  and  $[\text{NPCl}_2]_8$  was very small.

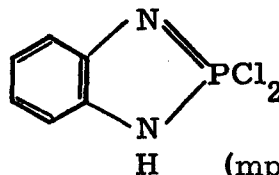
With  $[\text{C}_2\text{H}_5\text{NH}_3]\text{Cl}$  a similar reaction was observed.

Aniline reacted smoothly with  $\text{NP}_2\text{Cl}_7$ . However, the yield of LXVI was small. Compound LXVII was formed besides LXVI.



(m. p. 179°)

LXVII

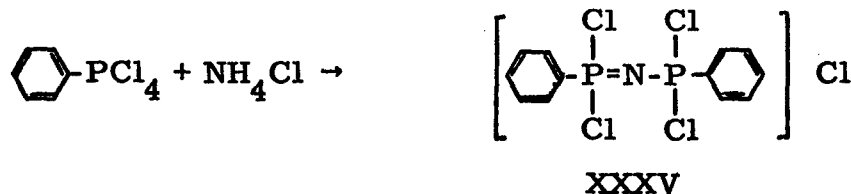


(mp 216° decomp)

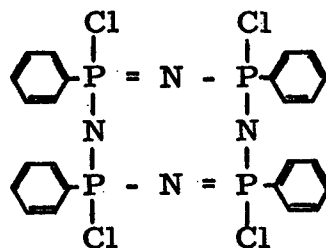
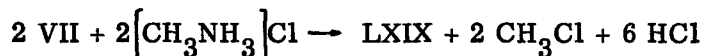
LXVIII

o-Phenylenediamine and  $\text{NP}_2\text{Cl}_7$  formed compound LXVIII and no polymeric phosphonitrilic chlorides. By the reaction of cyclohexylamine and  $\text{NP}_2\text{Cl}_7$  a crystalline compound  $[\text{C}_6\text{H}_{12}\text{N}_2\text{P}_2\text{Cl}_6]_2$  was prepared. We tried to elucidate the structure of this compound, but we did not succeed.

Further, we prepared compound XXXV. This substance was obtained by the reaction



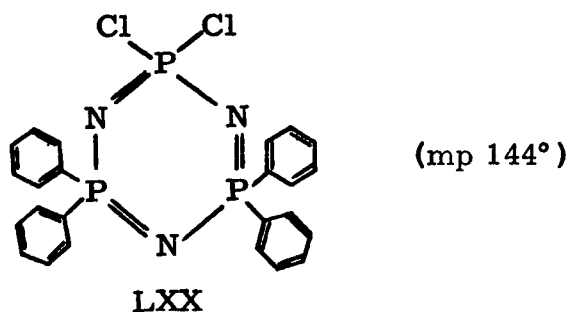
The reaction of this compound XXV with  $\text{NP}_2\text{Cl}_7$  was studied. The reaction was observed:



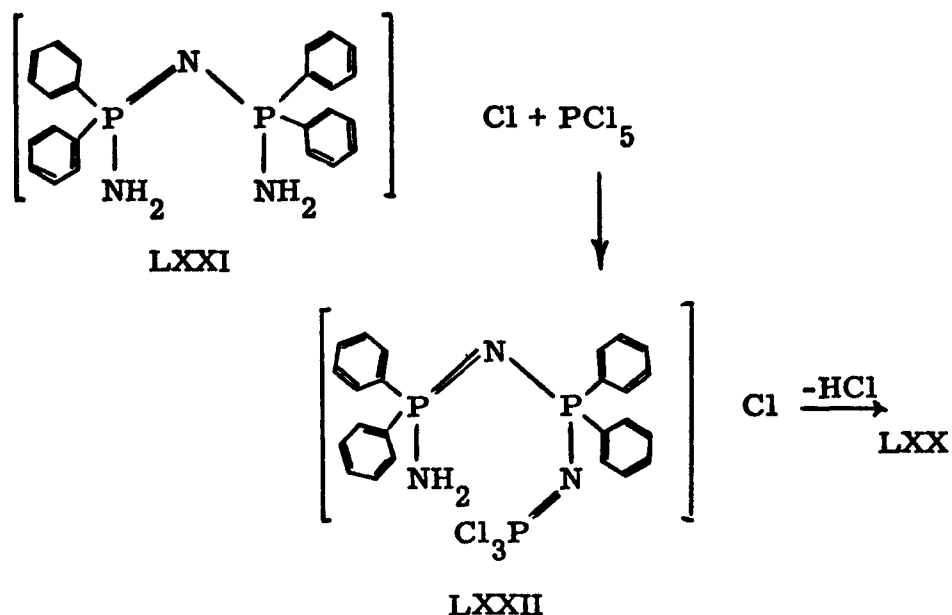
LXIX

Only one of the possible 4 isomers of LXIX was formed, e.g., a compound with mp 248°.

To summarize, a good method for the preparation of tetrameric phosphonitrilic compounds was found. Other polymers were not obtained in good yield. Further, a method for the preparation of compound LXX was developed.



This compound LXX was obtained by reaction of LXXI (Reference 21) with  $\text{PCl}_5$ . We were able to obtain LXX in better yield when tetrachloroethane was used as a solvent. We were able to show that the first reaction product was LXXII. At 120° to 130° (5 hours) ring closure was obtained and LXX was formed.



The preparation of other derivatives of phosphorus nitrilic chlorides, e.g., LXI and LXII was already mentioned.



## REFERENCES

1. G. J. Perkatsch, I. N. Shmurova, A. V. Kirsanov, V. J. Schewtschenko, A. S. Schtepanek: Phosphazo-Verbindungen, Editors: Naukova Dumka, Kiev, 1965.
2. Michaelis, Liebigs Annalen d. Chemie, 326, 129 (1903); 407, 290 (1915).
3. S. Trippett, J. Chem. Soc. (London), 1962, 4731.
4. I. N. Shmurova and A. V. Kirsanov, Zhur. obshchei Khim., 30, 3044 (1960).
5. A. C. Chapman, W. S. Holmes, N. L. Paddock, and H. T. Searle, J. Chem. Soc. (London), 1961, 1825.
6. E. Fluck: Die kernmagnetische Resonanz und ihre Anwendung in der Anorganischen Chemie., Springer-Verlag, Heidelberg, 1963.
7. P. A. Fowell and C. T. Mortimer, Chemistry and Industry, 1960, 444.
8. H. Hess and D. Forst, Z. anorg. allg. Chem., 342, 240 (1966).
9. Compare Alkyl Thiophosphonic Esters: H. Finegold, J. Am. Chem. Soc., 82, 2641 (1960); Ann. N. Y. Acad. Sci., 70, 875 (1958).
10. L. Parts, M. L. Nielsen and J. T. Miller, Jr., Inorg. Chem., 3, 1261 (1964).
11. M. Becke-Goehring and L. Leichner, Angew. Chem., 76, 686 (1964).
12. H. Ulrich and A. A. R. Sayigh, Angew. Chem., 76, 647 (1964).
13. M. Becke-Goehring, Th. Mann and H. D. Euler, Chem. Ber., 94, 193 (1961).
14. M. Becke-Goehring, A. Debo, E. Fluck and W. Goetze, Chem. Ber., 94, 1383 (1961).
15. M. Becke-Goehring, W. Gehrman and W. Goetze, Z. anorg. allg. Chem., 326, 127 (1963).
16. Compare A. V. Kirsanov, Nachr. Akad. Wiss. UdSSR, Abt. Chem. Wiss. 1950, 426; ebenda, 1954, 646; J. allg. Chem., 22, 1346 (1952); I. N. Shmurova and A. V. Kirsanov, J. angew. Chem. 30, 3044 (1960).
17. Concerning the possibility of this dissociation, compare with M. Becke-Goehring and W. Lehr, Chem. Ber., 94, 1591 (1961).
18. Concerning the existence of such intermediates, compare with W. J. Schentschenko, N. D. Bondartschuk, and A. V. Kirsanov, Zhur. Obsh. Khim., 33, 1342 (1963).
19. A. V. Kirsanov and I. N. Shmurova, Zhur. Obsh. Khim., 28, 2478 (1958).
20. M. Becke-Goehring and W. Lehr, Z. anorg. allg. Chem., 325, 287 (1963).
21. D. L. Herring and C. M. Douglas, Inorg. Chem., 3, 429 (1964).

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)

University of Heidelberg  
Heidelberg, Germany

2a. REPORT SECURITY CLASSIFICATION

UNCLASSIFIED

2b. GROUP

3. REPORT TITLE

NITROGEN-PHOSPHORUS POLYMERS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Summary Report Oct. 1964 - June 1966

5. AUTHOR(S) (Last name, first name, initial)

Becke-Goehring, Margot

6. REPORT DATE

November 1966

7a. TOTAL NO. OF PAGES

43

7b. NO. OF REFS

21

8a. CONTRACT OR GRANT NO. AF 61(052)-682

a. PROJECT NO. 7342

c. Task No. 734201

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

AFML-TR-64-417, Part II

10. AVAILABILITY/LIMITATION NOTICES

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

Air Force Materials Laboratory, Research  
and Technology Div., Air Force Systems  
Command, Wright-Patterson AFB, Ohio, 45433

13. ABSTRACT

A variety of chemical systems containing phosphorus nitrogen bands have been investigated as potential intermediates for the synthesis of polymeric materials having extreme thermal and chemical stability. These investigations include the preparation and reactions of a variety of compounds with four-membered ring systems containing alternate P and N atoms, compounds with four-membered ring systems containing P, N and C atoms, and compounds containing P-N-P chains; and the preparation of phosphonitrilic chlorides and their derivatives.

DD FORM 1 JAN 64 1473

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Phosphonitrilic Halides Monomers Inorganic Polymers Thermally Stable Polymers Phosphorus Nitride Salts Phosphorus Compounds Diamines						

### INSTRUCTIONS

**1. ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

**2a. REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

**2b. GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

**3. REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

**4. DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

**5. AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

**6. REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

**7a. TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

**7b. NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

**8a. CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

**8b, 8c, & 8d. PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

**9a. ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

**9b. OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

**10. AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through \_\_\_\_\_."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through \_\_\_\_\_."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through \_\_\_\_\_."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

**11. SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

**12. SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

**13. ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

**14. KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.